



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C08L 23/10	A1	(11) International Publication Number: WO 00/11076 (43) International Publication Date: 2 March 2000 (02.03.00)
(21) International Application Number: PCT/EP99/05262 (22) International Filing Date: 23 July 1999 (23.07.99) (30) Priority Data: 98202800.3 20 August 1998 (20.08.98) EP (71) Applicant (for all designated States except US): MONTECH USA INC. [US/US]; Suite 1704, 300 Delaware Avenue, Wilmington, DE 19803 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): PELLICONI, Anteo [IT/IT]; Via Volta, 22, I-44030 S. M. Maddalena (IT). FERRARI, Paolo [IT/IT]; Via Scandiana, 24A, I-44100 Ferrara (IT). (74) Agent: GAVERINI, Gaetano; Montell Italia S.p.A., Via Pergolesi, 25, I-20124 Milano (IT).		(81) Designated States: AU, BR, CA, CN, CZ, HU, ID, IL, IN, JP, KR, MX, NO, PL, SG, UA, US, ZA, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: CRYSTALLINE PROPYLENE COPOLYMER COMPOSITIONS HAVING IMPROVED SEALABILITY AND OPTICAL PROPERTIES AND REDUCED SOLUBILITY (57) Abstract A crystalline propylene copolymer composition having MFR L values from 2 to 15 g/10 min. and comprising (percent by weight): A) 20–80 % of one or more propylene copolymers; B) 20–80 % of one or more propylene copolymers with different comonomer(s) content than in A); the said MFR L values (MFR L (2)) being obtained by subjecting to degradation a precursor composition comprising the same components A) and B) in the above said proportions, but having MFR L values (MFR L (1)) from 0.3 to 5 g/10 min., with a ratio MFR L (2) to MFR L (1) of from 2 to 20.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

CRYSTALLINE PROPYLENE COPOLYMER COMPOSITIONS HAVING IMPROVED SEALABILITY AND OPTICAL PROPERTIES AND REDUCED SOLUBILITY.

The present invention relates to crystalline propylene copolymer compositions useful in the preparation of heat-sealable films, sheets and films thereof and to a process for preparing said compositions.

Crystalline copolymers of propylene with other olefins (mainly ethylene, 1-butene or both), or mixtures of such copolymers with other olefin polymers are known in the prior art as heat-sealable materials.

These crystalline copolymers are obtained by polymerizing propylene with minor amounts of other olefin comonomers in the presence of coordination catalysts.

The polymerized comonomer units are statistically distributed in the resulting copolymer and the melting point of said copolymers results to be lower than the melting point of crystalline propylene homopolymers. Also the seal initiation temperature (as later defined in detail) of the said copolymers results to be favorably low.

However, the introduction of the comonomer units adversely affects the crystal structure of the polymer, resulting in relatively large quantities of a polymer fraction soluble in organic solvents, so that the copolymers having a particularly low seal initiation temperature cannot be used in the field of food packaging.

Many technical solutions are disclosed in the prior art in order to find a good balance between heat-sealability (as demonstrated by low seal initiation temperatures) and solubility. In particular, published European patent application 483523 discloses compositions prepared directly in a polymerization process, having a low seal initiation temperature and a low content of a fraction soluble in xylene at room temperature or in n-hexane at 50 °C. These compositions comprise (by weight):

- 30-60% of a copolymer of propylene and a C₄-C₈ alpha-olefin, containing 80-98% of propylene;
- 35-70% of a copolymer of propylene with ethylene and optionally 1-10% of a C₄-C₈ alpha-olefin, wherein the content of ethylene is 5-10% when the C₄-C₈ alpha-olefin is not present, or 0.5-5% when the C₄-C₈ alpha-olefin is present.

Published European patent application 674991 discloses other compositions prepared directly in a polymerization process, having a good ink adhesion in addition to a low seal

initiation temperature and low content of a polymer fraction soluble in organic solvents. These compositions comprise (by weight):

- 20-60% of a copolymer of propylene with ethylene, containing 1 to 5% of ethylene;
- 40-80% of a copolymer of propylene with ethylene and a C₄-C₈ alpha-olefin, the ethylene content being 1-5% and the C₄-C₈ alpha-olefin content being 6-15%;

the total content of ethylene in the compositions being 1-5% and the total content of C₄-C₈ alpha-olefin in the compositions being 2.4-12%.

Other heat-sealable compositions, comprising two different kinds of copolymers of propylene with higher alpha-olefins, are disclosed in the published European patent application 560326.

On the other hand, it is known that, in general, the Melt Flow Rate (MFR) of an olefin polymer can be adjusted by degradation, in particular by treatment at elevated temperatures in the presence of an initiator of free radicals ("visbreaking" treatment).

In the field of heat-sealable olefin copolymers it is also known that the said degradation treatment can improve the heat-seal, optical and solubility properties, as explained in particular in US patent 5,246,769 and in the Japanese published patent application Sho 59-117506.

However, in these two documents the degradation treatment is applied to single copolymers of propylene with ethylene and/or higher alpha-olefins, resulting into a still high seal initiation temperature.

An attempt to apply the degradation treatment to heat-sealable compositions comprising two copolymers of propylene with ethylene and/or higher alpha-olefins is disclosed in the published European patent application 203727. In this case a copolymer of propylene with 25-45% by weight of butene-1 is first subjected to the degradation treatment and then blended with another copolymer of propylene with ethylene and/or butene-1.

However, while the seal initiation temperature and the haze values are brought to satisfactory levels, the content of fraction soluble in organic solvents results to be high (25 °C xylene-soluble fraction contents of around 30% are considered to be satisfactory).

It has now surprisingly been found that a particularly valuable balance of heat-sealability, low content of a fraction soluble in organic solvents and optical properties (in particular a very low Haze) is obtained by subjecting specific crystalline propylene copolymer compositions to a degradation treatment.

Therefore the present invention provides crystalline propylene copolymer compositions having MFR L values from 2 to 15 g/10 min., preferably from 3 to 15 g/10 min., more preferably from 4 to 10 g /10 min., and comprising (percent by weight):

- A) 20-80%, preferably 20-60%, more preferably 30-50%, of one or more propylene copolymers selected from the group consisting of (A 1) propylene/ethylene copolymers containing 1-7% of ethylene; (A 2) copolymers of propylene with one or more C₄-C₈ alpha-olefins, containing 2-10% of the C₄-C₈ alpha-olefins; (A 3) copolymers of propylene with ethylene and one or more C₄-C₈ alpha-olefins, containing 0.5-4.5% of ethylene and 2-6% of C₄-C₈ alpha-olefins, provided that the total content of ethylene and C₄-C₈ alpha-olefins in (A 3) be equal to or lower than 6.5%;
- B) 20-80%, preferably 40-80%, more preferably 50-70%, of one or more propylene copolymers selected from the group consisting of (B 1) copolymers of propylene with one or more C₄-C₈ alpha-olefins, containing from more than 10% to 30% of C₄-C₈ alpha-olefins; (B 2) copolymers of propylene with ethylene and one or more C₄-C₈ alpha-olefins, containing 1-7% of ethylene and 6-15% of C₄-C₈ alpha-olefins;

the said MFR L values (MFR L (2)) being obtained by subjecting to degradation a precursor composition comprising the same components A) and B) in the above said proportions, but having MFR L values (MFR L (1)) from 0.3 to 5 g/10 min., preferably from 0.5 to 3 g/10 min., with a ratio MFR L (2) to MFR L (1) of from 2 to 20, preferably from 3 to 15.

From the above definitions it is evident that the term "copolymer" includes polymers containing more than one kind of comonomers.

As previously said, the compositions of the present invention have low seal initiation temperatures (preferably lower than 100 °C), a low content of a fraction soluble or extractable in organic solvents (preferably equal to or lower than 20% by weight in xylene at 25 °C and equal to or lower than 5% by weight in n-hexane at 50 °C), and very low haze values (preferably lower than 1%, more preferably equal to or lower than 0.5%, measured on films according to the method described in the examples).

The melting temperature of said composition is preferably from about 126 to 147 °C.

Moreover, the compositions of the present invention can be obtained by an efficient and inexpensive process (constituting a further object of the present invention), comprising the following stages:

- 1) preparing the previously said precursor composition by polymerizing the monomers in at least two sequential steps, wherein components A) and B) are prepared in separate subsequent steps, operating in each step in the presence of the polymer formed and the catalyst used in the preceding step, and dosing the molecular weight regulator (preferably hydrogen) in such amounts as to obtain a MFR L (1) value for the precursor composition of from 0.3 to 5 g/10 min., preferably from 0.5 to 3 g/10 min.;
- 2) subjecting the precursor composition obtained in 1) to a degradation treatment in order to obtain MFR L (2) values for the final composition from 3 to 15 g/10 min. preferably from 4 to 10 g/10 min., with a degradation ratio, in terms of ratio MFR L (2) to MFR L (1), of from 2 to 20, preferably from 3 to 15.

Such a preferred process is extremely convenient, as it avoids the separate preparation of the components of the precursor composition and separate degradation treatments.

From the preceding description it should be clear that in the precursor composition the comonomer content and relative amounts of components A) and B) are the same as in the final composition (after degradation). The degradation treatment has the effect of increasing the MFR L values of the composition from MFR L (1) to MFR L (2), with the said values of the ratio between the two MFR L values, namely MFR L (2)/MFR L (1), of from 2 to 20.

The above said MFR L values are measured according to ASTM D 1238 L.

In both the precursor and the final compositions the MFR L values of the components A) and B) are not particularly critical, provided that the MFR L values of the total compositions fall within the said ranges.

Indicatively, in the precursor composition the MFR L value of both A) and B) can be from 0.1 to 10 g/10 min..

Preferred comonomer contents in the compositions of the present invention are (by weight):

- 2-4% of ethylene for (A 1);
- 4-8% of one or more C₄-C₈ alpha-olefins for (A 2);
- 1-4% of ethylene and 2-5% of one or more C₄-C₈ alpha-olefins, with a total content of ethylene and C₄-C₈ alpha-olefins equal to or lower than 6%, for (A 3);
- 11-20% of one or more C₄-C₈ alpha-olefins for (B 1);
- 2-4% of ethylene and 7-12% of one or more C₄-C₈ alpha-olefins for (B 2).

Moreover, when an optimal ink adhesion is desired, the compositions of the present invention should comprise a component (A 1) and a component (B 2) in the previously said

relative amounts, while the total content of ethylene in the compositions should be 1-5%, preferably 2-4% by weight and the total content of C₄-C₈ alpha-olefins in the same compositions should be 2.4-12%, preferably 3.5-8.4% by weight.

Examples of C₄-C₈ alpha olefins are 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene and 1-octene. Particularly preferred is 1-butene.

As previously explained, the precursor compositions can be prepared by sequential polymerization. Such polymerization is carried out in the presence of stereospecific Ziegler-Natta catalysts. An essential component of said catalysts is a solid catalyst component comprising a titanium compound having at least one titanium-halogen bond, and an electron-donor compound, both supported on a magnesium halide in active form. Another essential component (co-catalyst) is an organoaluminum compound, such as an aluminum alkyl compound.

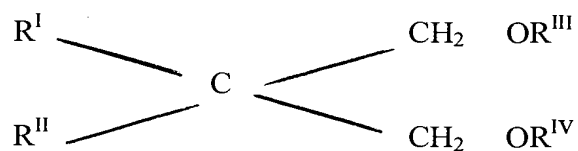
An external donor is optionally added.

The catalysts generally used in the process of the invention are capable of producing polypropylene with an isotactic index greater than 90%, preferably greater than 95%. Catalysts having the above mentioned characteristics are well known in the patent literature; particularly advantageous are the catalysts described in US patent 4,399,054 and European patent 45977.

The solid catalyst components used in said catalysts comprise, as electron-donors (internal donors), compounds selected from the group consisting of ethers, ketones, lactones, compounds containing N, P and/or S atoms, and esters of mono- and dicarboxylic acids.

Particularly suitable electron-donor compounds are phthalic acid esters, such as diisobutyl, dioctyl, diphenyl and benzylbutyl phthalate.

Other electron-donors particularly suitable are 1,3-diethers of formula:



wherein R^I and R^{II} are the same or different and are C₁-C₁₈ alkyl, C₃-C₁₈ cycloalkyl or C₇-C₁₈ aryl radicals; R^{III} and R^{IV} are the same or different and are C₁-C₄ alkyl radicals; or are the 1,3-diethers in which the carbon atom in position 2 belongs to a cyclic or polycyclic structure made up of 5, 6 or 7 carbon atoms and containing two or three unsaturations.

Ethers of this type are described in published European patent applications 361493 and 728769.

Representative examples of said dieters are 2-methyl-2-isopropyl-1,3-dimethoxypropane, 2,2-diisobutyl-1,3-dimethoxypropane, 2-isopropyl-2-cyclopentyl-1,3-dimethoxypropane, 2-isopropyl-2-isoamyl-1,3-dimethoxypropane, 9,9-bis (methoxymethyl) fluorene.

The preparation of the above mentioned catalyst components is carried out according to various methods.

For example, a $\text{MgCl}_2 \cdot n\text{ROH}$ adduct (in particular in the form of spheroidal particles) wherein n is generally from 1 to 3 and ROH is ethanol, butanol or isobutanol, is reacted with an excess of TiCl_4 containing the electron-donor compound. The reaction temperature is generally from 80 to 120 °C. The solid is then isolated and reacted once more with TiCl_4 , in the presence or absence of the electron-donor compound, after which it is separated and washed with aliquots of a hydrocarbon until all chlorine ions have disappeared.

In the solid catalyst component the titanium compound, expressed as Ti, is generally present in an amount from 0.5 to 10% by weight. The quantity of electron-donor compound which remains fixed on the solid catalyst component generally is 5 to 20% by moles with respect to the magnesium dihalide.

The titanium compounds which can be used for the preparation of the solid catalyst component are the halides and the halogen alcoholates of titanium. Titanium tetrachloride is the preferred compound.

The reactions described above result in the formation of a magnesium halide in active form. Other reactions are known in the literature, which cause the formation of magnesium halide in active form starting from magnesium compounds other than halides, such as magnesium carboxylates.

The active form of magnesium halide in the solid catalyst component can be recognized by the fact that in the X-ray spectrum of the catalyst component the maximum intensity reflection appearing in the spectrum of the nonactivated magnesium halide (having a surface area smaller than 3 m²/g) is no longer present, but in its place there is a halo with the maximum intensity shifted with respect to the position of the maximum intensity reflection of the nonactivated magnesium dihalide, or by the fact that the maximum intensity reflection shows a width at half-peak at least 30% greater than the one of the maximum intensity reflection which appears in the spectrum of the nonactivated magnesium halide. The most

active forms are those where the above mentioned halo appears in the X-ray spectrum of the solid catalyst component.

Among magnesium halides, the magnesium chloride is preferred. In the case of the most active forms of magnesium chloride, the X-ray spectrum of the solid catalyst component shows a halo instead of the reflection which in the spectrum of the nonactivated chloride appears at 2.56 Å.

The Al-alkyl compounds used as co-catalysts comprise the Al-trialkyls, such as Al-triethyl, Al-triisobutyl, Al-tri-n-butyl, and linear or cyclic Al-alkyl compounds containing two or more Al atoms bonded to each other by way of O or N atoms, or SO₄ or SO₃ groups.

The Al-alkyl compound is generally used in such a quantity that the Al/Ti ratio be from 1 to 1000.

The electron-donor compounds that can be used as external donors include aromatic acid esters such as alkyl benzoates, and in particular silicon compounds containing at least one Si-OR bond, where R is a hydrocarbon radical.

Examples of silicon compounds are (tert-butyl)₂ Si (OCH₃)₂, (cyclohexyl) (methyl) Si (OCH₃)₂, (phenyl)₂ Si (OCH₃)₂ and (cyclopentyl)₂ Si (OCH₃)₂. 1,3-diethers having the formulae described above can also be used advantageously. If the internal donor is one of these diethers, the external donors can be omitted.

As previously said, the polymerization stage can be carried out in at least two sequential steps, wherein components A) and B) are prepared in separate subsequent steps, operating in each step, except the first step, in the presence of the polymer formed and the catalyst used in the preceding step. The catalyst is added only in the first step, however its activity is such that it is still active for all the subsequent steps.

The order in which components A) and B) are prepared is not critical.

The polymerization stage, which can be continuous or batch, is carried out following known techniques and operating in liquid phase, in the presence or not of inert diluent, or in gas phase, or by mixed liquid-gas techniques. It is preferable to carry out the polymerization in gas phase.

Reaction time, pressure and temperature relative to the two steps are not critical, however it is best if the temperature is from 20 to 100 °C. The pressure can be atmospheric or higher.

The regulation of the molecular weight is carried out by using known regulators, hydrogen in particular.

The catalysts can be pre-contacted with small amounts of olefins (prepolymerization).

Specific examples of precursor compositions suited for the obtainment of the compositions of the present invention by a degradation treatment, and of polymerization processes for preparing the said precursor compositions, are disclosed in the already cited published European patent applications 483523, 560326 and 674991.

The degradation treatment can be carried out by any means and under the conditions known in the art to be effective in reducing the molecular weight of olefin polymers.

In particular it is known that the molecular weight of olefin polymers can be reduced by application of heat (thermal degradation), preferably in the presence of initiators of free radicals, like ionizing radiations or chemical initiators.

Particularly preferred among the chemical initiators are the organic peroxides, specific examples of which are 2,5-dimethyl-2,5-di (t-butylperoxy) hexane and dicumyl-peroxide.

The degradation treatment with the chemical initiators can be carried out in the conventional apparatuses generally used for processing polymers in the molten state, like in particular single or twin screw extruders. It is preferred to operate under inert atmosphere, for instance under nitrogen.

The amount of chemical initiator to be added to the precursor composition can be easily determined by one skilled in the art, based upon the MFR L (1) value (i.e. the MFR L value of the precursor composition) and the desired MFR L (2) value (i.e. the MFR L value of the final composition). Generally such amount is comprised in the range of from 100 to 700 ppm.

The degradation temperature is preferably in the range of from 180 to 300 °C.

The compositions of the present invention can also contain additives commonly employed in the art, such as antioxidants, light stabilizers, heat stabilizers, colorants and fillers.

Among the various applications made possible by the previously described properties, the compositions of the present invention are particularly useful for the preparation of films and sheets.

Films are generally characterized by a thickness of less than 100 µm, while sheets have generally a thickness greater than or equal to 100 µm.

Both films and sheets can be mono- or multilayer.

In the case of multilayer films or sheets, at least one layer comprises the compositions of the present invention. Each layer that does not comprise the compositions of the present invention can be composed of other olefin polymers, such as polypropylene or polyethylene.

Generally speaking, the films and sheets of this invention can be prepared by known techniques, such as extrusion and calendering. Specific examples of films containing the compositions of the present invention are disclosed hereinafter in the test for determining the seal initiation temperature (S.I.T.).

The particulars are given in the following examples, which are given to illustrate, without limiting, the present invention.

Examples 1 and 2 (Comparative)

In the following Example 1 a precursor composition is prepared by sequential polymerization and then subjected to degradation to obtain a final composition according to the invention. For comparison purpose, in Example 2 a composition having a seal initiation temperature of less than 100 °C and a MFR L value comparable to the value obtained in Example 1 by degradation, is prepared directly in polymerization.

The solid catalyst component used in polymerization is a highly stereospecific Ziegler-Natta catalyst component supported on magnesium chloride, containing about 2.5% by weight of titanium and diisobutylphthalate as internal donor, prepared by analogy with the method described in the examples of European published patent application 674991.

CATALYST SYSTEM AND PREPOLYMERIZATION TREATMENT

Before introducing it into the polymerization reactors, the solid catalyst component described above is contacted at -5 °C for 5 minutes with aluminum triethyl (TEAL) and dicyclopentyldimethoxysilane (DCPMS), in a TEAL/DCPMS weight ratio equal to about 4 and in such quantity that the TEAL/Ti molar ratio be equal to 65.

The catalyst system is then subjected to prepolymerization by maintaining it in suspension in liquid propylene at 20 °C for about 20 minutes before introducing it into the first polymerization reactor.

POLYMERIZATION

Into a first gas phase polymerization reactor a propylene/ethylene copolymer (component (A)) is produced by feeding in a continuous and constant flow the prepolymerized catalyst system, hydrogen (used as molecular weight regulator) and propylene and ethylene monomers in the gas state.

Polymerization conditions, molar ratio of the reactants, and composition of the copolymers obtained are shown in Table 1.

The copolymer produced in the first reactor, constituting 35% by weight of the total composition in Example 1 and 40% by weight of the total composition in Example 2, is

discharged in a continuous flow and, after having been purged of unreacted monomers, is introduced in a continuous flow into the second gas phase reactor, together with quantitatively constant flows of hydrogen and propylene, ethylene and 1-butene monomers in the gas state.

The propylene/ethylene/1-butene copolymer formed in the second reactor (component (B)) is produced in a quantity equal to 65% by weight with respect to the total composition in Example 1 and 60% by weight with respect to the total composition in Example 2. Polymerization conditions, molar ratio of the reactants and composition of the copolymers obtained are shown in Table 1.

The polymer particles exiting the second reactor are subjected to a steam treatment to remove the reactive monomers and volatile substances, and then dried.

Then the polymer particles are introduced in a rotating drum, where they are mixed with 0.05% by weight of paraffin oil ROL/OB 30 (having a density of 0.842 kg/l at 20 °C according to ASTM D 1298 and flowing point of -10 °C according to ASTM D 97), 0.15% by weight of Irganox B 215 (made of about 66% by weight of tri [2,4-di-t-butyl-phenyl] phosphite and complement to 100% of tetrakis [methylene (3,5-di-t-butyl-4-hydroxy-hydrocinnamate)]) and 0.05% by weight of calcium stearate.

To a portion of the polymer particles of Example 1, constituting the precursor composition, are also added 300 ppm of Luperox 101 (2,5-dimethyl-2,5-di (t-butylperoxy) hexane), which acts as initiator of free radicals in the subsequent extrusion treatment.

Then the polymer particles are introduced in a twin screw extruder Berstorff ZE 25 (length/diameter ratio of screws: 33) and extruded under nitrogen atmosphere in the following conditions:

Rotation speed:	250 rpm;
Extruder output:	6-20 kg/hour;
Melt temperature:	200-250 °C.

The data relating to the polymer compositions reported in Tables 1 and 2 are obtained from measurements carried out on the so extruded polymers. The data reported in Table 2 relate to the final composition according to the present invention, obtained by subjecting to degradation the precursor composition of Example 1, namely by extruding it with 300 ppm of Luperox 101 as described above.

The data shown in the tables are obtained by using the following test methods.

- **Molar ratios of the feed gases**

Determined by gas-chromatography.

- **Ethylene and 1-butene content of the polymers**

Determined by I.R. spectroscopy.

- **Melt Flow Rate MFR L**

Determined according to ASTM D 1238, condition L.

- **Melting temperature (T_m) and crystallization temperature (T_c)**

Determined by DSC (Differential Scanning Calorimetry).

- **Xylene soluble fraction**

Determined as follows.

2.5 g of polymer and 250 cm³ of xylene are introduced in a glass flask equipped with a refrigerator and a magnetical stirrer. The temperature is raised in 30 minutes up to the boiling point of the solvent. The so obtained clear solution is then kept under reflux and stirring for further 30 minutes. The closed flask is then kept for 30 minutes in a bath of ice and water and in thermostatic water bath at 25 °C for 30 minutes as well. The so formed solid is filtered on quick filtering paper. 100 cm³ of the filtered liquid is poured in a previously weighed aluminum container which is heated on a heating plate under nitrogen flow, to remove the solvent by evaporation. The container is then kept in an oven at 80 °C under vacuum until constant weight is obtained.

- **Hexane soluble fraction**

Determined according to FDA 177, 1520, by suspending in an excess of hexane a 100 µm thick film specimen of the composition being analyzed, in an autoclave at 50 °C for 2 hours. Then the hexane is removed by evaporation and the dried residue is weighed.

- **Seal Initiation Temperature (S.I.T.)**

Determined as follows.

Preparation of the film specimens

Some films with a thickness of 50 µm are prepared by extruding each test composition in a single screw Collin extruder (length/diameter ratio of screw: 25) at a film drawing speed of 7 m/min. and a melt temperature of 210-250 °C. Each resulting film is superimposed on a 1000 µm thick film of a propylene homopolymer having an isotacticity index of 97 and a MFR L of 2 g/10 min. The superimposed films are bonded to each other in a Carver press at 200 °C under a 9000 kg load, which is maintained for 5 minutes.

The resulting laminates are stretched longitudinally and transversally, i.e. biaxially, by a factor 6 with a TM Long film stretcher at 150 °C, thus obtaining a 20 µm thick film (18 µm homopolymer + 2 µm test composition).

2 x 5 cm specimens are cut from the films.

Determination of the S.I.T.

For each test two of the above specimens are superimposed in alignment, the adjacent layers being layers of the particular test composition. The superimposed specimens are sealed along one of the 5 cm sides with a Brugger Feinmechanik Sealer, model HSG-ETK 745. Sealing time is 0.5 seconds at a pressure of 0.1 N/mm². The sealing temperature is increased for each seal, starting from about 10 °C less than the melting temperature of the test composition. The sealed samples are left to cool and then their unsealed ends are attached to an Instron machine where they are tested at a traction speed of 50 mm/min..

The S.I.T. is the minimum sealing temperature at which the seal does not break when a load of at least 2 Newtons is applied in the said test conditions.

- Haze on film

Determined on 50 µm thick films of the test composition, prepared as described for the S.I.T. test. The measurement is carried out on a 50 x 50 mm portion cut from the central zone of the film.

The instrument used for the test is a Gardner photometer with Haze-meter UX-10 equipped with a G.E. 1209 lamp and filter C. The instrument calibration is made by carrying out a measurement in the absence of the sample (0% Haze) and a measurement with intercepted light beam (100% Haze).

- Gloss on film

Determined on the same specimens as for the Haze.

The instrument used for the test is a model 1020 Zehntner photometer for incident measurements. The calibration is made by carrying out a measurement at incidence angle of 60 ° on black glass having a standard Gloss of 96.2% and a measurement at an incidence angle of 45 ° on black glass having a standard Gloss of 55.4%.

Table 1

EXAMPLES	1	2 (comp.)
<u>1st REACTOR</u>		
Temperature, °C	70	70
Pressure, Mpa	1.8	1.6
H ₂ /C ₃ ⁻ , mol.	< 0.01	0.04
C ₂ ⁻ /C ₂ ⁻ + C ₃ ⁻ , mol.	0.03	0.03
<u>RESULTING POLYMER</u>		
C ₂ ⁻ , %	3.1	3.1
MFR L, g/10 min.	0.54	5.0
<u>2nd REACTOR</u>		
Temperature, °C	65	65
Pressure, Mpa	1.6	1.6
H ₂ /C ₃ ⁻ , mol.	0.021	0.13
C ₂ ⁻ /C ₂ ⁻ + C ₃ ⁻ , mol.	0.03	0.03
C ₄ ⁻ /C ₄ ⁻ + C ₃ ⁻ , mol.	0.17	0.17
<u>TOTAL COMPOSITION</u>		
C ₂ ⁻ , %	4.0	4.0
C ₄ ⁻ , %	6.0	5.8
MFR L, g/10 min.	0.98	4.4
Tm/Tc, °C	136/88.7	134/87.7

Table 1 (cont.)

EXAMPLES	1	2 (comp.)
X.S., %	11.9	15.1
H.S., %	3.9	7.0
C ₂ ⁻ in X.I., %	3.2	-
C ₄ ⁻ in X.I., %	5.6	-
C ₂ ⁻ in X.S., %	10.9	-
C ₄ ⁻ in X.S., %	8.9	-
S.I.T., °C	97	97
Haze, %	11.9	1.9
Gloss, %	66.2	80.0

Table 2
(Example 1)

TOTAL COMPOSITION	
C ₂ ⁻ , %	4.0
C ₄ ⁻ , %	6.0
MFR L, g/10 min.	5.7
T _m /T _c , °C	137/89.7
X.S., %	11.9
H.S., %	3.8
C ₂ ⁻ in X.I., %	3
C ₄ ⁻ in X.I., %	4.6
C ₂ ⁻ in X.S., %	6.6
C ₄ ⁻ in X.S., %	9.8
S.I.T., °C	93
Haze, %	0.1
Gloss, %	88.5

Note to the tables:

C₂⁻ = ethylene; C₃⁻ = propylene; C₄⁻ = 1-butene; X.S. = Xylene Soluble fraction; H.S. = Hexane Soluble fraction; X.I. = Xylene Insoluble fraction; all percent amounts (except for Haze) are by weight.

From a comparison between the data of Table 2 and those of Example 2 (Comparative), reported in Table 1, it comes out that the balance of S.I.T., low solubility and optical properties of the compositions of the present invention is not achieved when a comparable value of MFR L is obtained directly in polymerization.

CLAIMS

1. A crystalline propylene copolymer composition having MFR L values from 2 to 15 g/10 min. and comprising (percent by weight):
 - A) 20-80% of one or more propylene copolymers selected from the group consisting of (A 1) propylene/ethylene copolymers containing 1-7% of ethylene; (A 2) copolymers of propylene with one or more C₄-C₈ alpha-olefins, containing 2-10% of the C₄-C₈ alpha-olefins; (A 3) copolymers of propylene with ethylene and one or more C₄-C₈ alpha-olefins, containing 0.5-4.5% of ethylene and 2-6% of C₄-C₈ alpha-olefins, provided that the total content of ethylene and C₄-C₈ alpha-olefins in (A 3) be equal to or lower than 6.5%;
 - B) 20-80% of one or more propylene copolymers selected from the group consisting of (B 1) copolymers of propylene with one or more C₄-C₈ alpha-olefins, containing from more than 10% to 30% of C₄-C₈ alpha-olefins; (B 2) copolymers of propylene with ethylene and one or more C₄-C₈ alpha-olefins, containing 1-7% of ethylene and 6-15% of C₄-C₈ alpha-olefins;

the said MFR L values (MFR L (2)) being obtained by subjecting to degradation a precursor composition comprising the same components A) and B) in the above said proportions, but having MFR L values (MFR L (1)) from 0.3 to 5 g/10 min., with a ratio MFR L (2) to MFR L (1) of from 2 to 20.
2. The crystalline propylene copolymer composition of claim 1, comprising (percent by weight):
 - A) 20-60% of a propylene/ethylene copolymer containing 1-7% of ethylene;
 - B) 40-80% of a copolymer of propylene with ethylene and one or more C₄-C₈ alpha-olefins, containing 1-7% of ethylene and 6-15% of C₄-C₈ alpha-olefins;

the total content of ethylene in the compositions being 1-5% and the total content of C₄-C₈ alpha-olefins in the composition being 2.4-12%.
3. A monolayer or multilayer film or sheet, wherein at least one layer comprises the crystalline propylene copolymer composition of claim 1.
4. A process for preparing the crystalline propylene copolymer composition of claim 1, comprising the following stages:
 - 1) preparing the precursor composition by polymerizing the monomers in at least two sequential steps, wherein components A) and B) are prepared in

- separate subsequent steps, operating in each step in the presence of the polymer formed and the catalyst used in the preceding step, and dosing the molecular weight regulator in such amounts as to obtain a MFR L (1) value for the precursor composition of from 0.3 to 5 g/10 min.;
- 2) subjecting the precursor composition obtained in 1) to a degradation treatment in order to obtain MFR L (2) values for the final composition from 3 to 15 g/10 min., with a degradation ratio, in terms of ratio MFR L (2) to MFR L (1), of from 2 to 20.
5. The process of claim 4, wherein the degradation ratio is from 3 to 15.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 99/05262

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08L23/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO 98 39384 A (EXXON CHEMICAL PATENTS INC) 11 September 1998 (1998-09-11) page 18, line 19 - page 19, line 8; claims; table 2 ---	1, 2, 4, 5
X	US 5 681 650 A (PEIFFER HERBERT ET AL) 28 October 1997 (1997-10-28) column 2, line 20 - line 22 column 2, line 58 - column 3, line 5 column 5, line 10 - line 31 column 6, line 1 - line 16 ---	1-3
A	EP 0 457 455 A (SHELL OIL CO) 21 November 1991 (1991-11-21) claims; table 2 -----	1-5



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

19 November 1999

Date of mailing of the international search report

01/12/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040. Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Clemente Garcia, R

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 99/05262

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9839384 A	11-09-1998	NONE	
US 5681650 A	28-10-1997	DE 4310684 A DE 59408381 D EP 0618070 A ES 2134867 T US 5508090 A	06-10-1994 15-07-1999 05-10-1994 16-10-1999 16-04-1996
EP 0457455 A	21-11-1991	AT 140016 T CA 2041898 A DE 69120601 D DE 69120601 T ES 2091289 T GR 3021152 T JP 5331327 A US 5362782 A	15-07-1996 15-11-1991 08-08-1996 02-01-1997 01-11-1996 31-12-1996 14-12-1993 08-11-1994